Scaled Quantum Mechanical (SQM) Force Field Calculations of the Hexathiometadiphosphate Anion $P_2S_6^{2-}$

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By *ab initio* quantum mechanical calculations on $P_2S_6^{2-}$ its equilibrium energy, geometry and vibrational frequencies along with their PED values have been obtained. The basis sets STO-5G, 6-31G, STO-5G* and 6-31G* were employed, and force field calculations were carried out at the STO-5G and the STO-5G* levels. The calculations show that the assignment for some bands between 180 and 260 cm^{-1} should be corrected. Two scaling factors were needed to fit the calculated frequencies with the observed frequencies within a deviation of less then 20 cm^{-1} for all vibrations, with the exception of $\nu_6(B_{1g})$. The calculated frequency of this vibration is very dependent on the polarization functions, and use of STO-2G for the 3d-orbitals corrects most of the deviation. STO-5G* and 6-31G* both give a good description of the geometry of the title ion, although STO-5G* yields a 0.04 Å too short terminal P–S distance.

Key words: Vibrational spectrum; Force field; Thiophosphate; $P_2S_6^{2-}$.

Introduction

Metal phosphorus sulphur compounds of the type $MePS_3$ (Me = Na, Ag, Tl) were first mentioned by Thilo and Ladwig [1]. For these compounds the authors proposed a polymeric chain structure in analogy to metaphosphate structures. Vibrational spectral investigations on similar solid and molten systems [2, 3] gave results contradictory to the proposed polymeric structure. Finally, crystal structure determinations of $MePS_3$ compounds (Me = Ag, Tl, K, Cs) [4–6] besides $Zn_4(P_2S_6)_3$ [7] proved the existence of $P_2S_6^{2-}$ units and hence justified the designation "hexathiometadiphosphate". The $P_2S_6^{2-}$ ion is isoelectronic to the Al_2Cl_6 molecule, and a temperature dependent dimer-monomer equilibrium has been formulated as [8]

$$P_2S_6^{2-} \rightleftharpoons 2\,PS_3^-$$

in agreement with the observations for Al_2Cl_6 [9, 10]. In this context Roesky et al. [11] have succeeded to prepare the uncommon PS_3^- ion in crystalline $[(C_6H_5)_4As]\,[PS_3]$.

An assignment of the vibrational frequencies of $P_2S_6^{2-}$ has already been carried out based on a normal coordinate analysis and in analogy with that of Al_2Cl_6 [12, 13]. HF-*ab initio* calculations of the vibrational frequencies have earlier been performed for PS_3^- [14] and recently for PS_3^- and PS_4^{3-} [15]. The results of the calculations [15] show that the assignment for PS_3^- had to be revised for the $\nu_2(A_2'')$ vibration, which was found to have a much lower vibrational frequency than earlier proposed [8, 11, 14]. We therefore began by *ab initio* calculations for $P_2S_6^{2-}$ [16] as well as for other large thiophosphate ions such as e.g. $P_2S_7^{4-}$ [17] in order to get reliable arguments for the assignment of their vibrational spectra.

Calculation Procedure

The Restricted-Hartree-Fock (RHF) *ab initio* calculations were performed with the program GAMESS [18] on Vax stations 3100 and 3200 and on a Silicon Graphics W25D workstation. For description of the calculation procedure and the basis sets, see e.g.

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Hinchcliffe [19, 20]. The total calculation time for the geometry optimizations and the numeric Hessian calculations on the Vax Station 3100 was ca. 24 CPU hours for STO-5G, and ca. 180 h for STO-5G*. Scaling of the force constants was done with the programs MOLVIB [21] and GAMFORCE [22]. The scaling of the interaction force constants was set to the logarithmic mean of the diagonal force constants involved. No optimization of the scaling force constants was performed. Geometry was also found for 6-31G*, but vibrational analysis was not carried out at this level as it would generate too large scratchfiles (more than 1 GB).

It appeared to be impossible for GAMESS [18] to produce a force field with only $3N-6=18$ internal coordinates, as the force field matrix then did not converge. We therefore ended up with a set of 24 coordinates, including the following (notation of the parameters in brackets):

All 4 $P-S_b$ stretches (R) and all 4 $P-S_t$ stretches (r) (S_b and S_t are bridging and terminal sulphur, respectively); one P–P stretch (β) (to account for the ring in-plane deformations); all 8 S_b-P-S_t bends (α); 2 S_t-P-S_t bends (θ); $S_b-P-P-S_b$ ring torsion (ζ); and 4 $S_t-P-P-S_t$ torsions (τ).

Results and Discussion

Table 1 gives the calculated geometry compared to the experimental one for the $P_2S_6^{2-}$ ion in crystalline $Cs_2P_2S_6$ [6]. The overall geometry (Figure 1) is rather good for all three calculations except that

i) there is a misfit of 3° in the $P-S_b-P$ angles, and
ii) there is an overestimation of the bond lengths of 0.10–0.17 Å when there are no polarization functions introduced.

As usual, the STO-nG basis sets (here STO-5G*) give an underestimation of the bond lengths, and the split valence (6-31) basis sets yield longer bonding distances [23]. It should also be noted that the split valence basis sets give weaker bridge bonds compared to the terminal bonds than the minimal basis sets, but the trend is reversed when polarization functions are introduced. In contrast, the energy of dissociation is almost unaffected by the polarization functions.

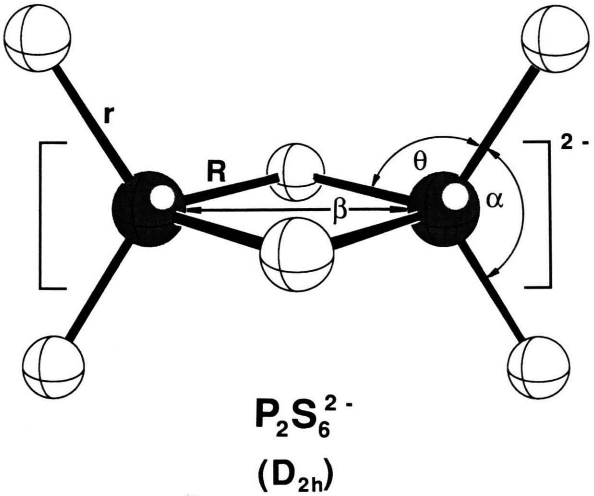

Fig. 1. Perspective ball and stick model giving the structure and the valence coordinate notation for the $P_2S_6^{2-}$ ion.

Table 1. Calculated and observed geometry and calculated equilibrium energy [Hartrees] and the different basis sets for the calculations or the hexametathiophosphate ion $P_2S_6^{2-}$.

Basis set[a]	STO-5G	6-31G	STO-5G*	STO-5G/2D	6-31G*	Experimental[b] [6]
1s	STO-5G	STO-6G	STO-5G	STO-5G	STO-6G	
2s, 2p	STO-3G	STO-6G	STO-3G	STO-3G	STO-6G	
3s, 3p	STO-3G	STO-3G	STO-3G	STO-3G	STO-3G	
3d			STO-1G	STO-2G	STO-1G	
4s, 4p		STO-1G			STO-1G	
Geometry						
$P-S_b$ [Å]	2.243	2.295	2.131	2.130	2.148	2.139
$P-S_t$ [Å]	2.104	2.125	1.927	1.918	1.991	1.967
$P-S_b-P$ [°]	90.9	91.7	90.3	90.4	90.8	87.1
S_t-P-S_t [°]	117.8	118.5	118.3	118.0	117.4	118.5
S_b-P-S_t [°]	111.6	111.5	111.3	111.4	111.7	110.9
Energy [E_h]	−3052.8889	−3066.3417	−3053.3319	−3053.3808	−3066.6514	
ΔE_D [kJ/mol]	−102	−246	−97		−250	

[a] Exponents for the STO-1G polarization functions (or 3d-orbitals): 0.65 and 0.55 for P and S, respectively.
[b] For $Cs_2P_2S_6$ [6]. Dimerization energy for the reaction $2\ PS_3^- \rightleftharpoons P_2S_6^{2-}$ [15].

Table 2. Calculated and observed vibrational frequencies (cm^{-1}) along with their assignment for $P_2S_6^{2-}$ ion with D_{2h} symmetry. *A*: Unscaled force field; *B*: Scaled force field, scaling factors given below; *C*: Deviation from experimental frequencies [6, 12]; *D*: Experimental frequencies.

STO-5G			STO-5G*				STO-5G/2D			Assignment (D_{2h})
A	B_1	*C*	*A*	B_2	B_3	*C*	*A*	B_3	*D* [6]	
34	43		34	28	28		33	28	44[a]	$\nu_{10}(B_{1u})$
91	104		112	94	94		113	94	118[a]	$\nu_5(A_u)$
144	164	− 5	181	151	151	−18	183	153	169 R, s	$\nu_4(A_g)$
167	193	+ 9	198	166	166	−16	190	159	184 R, s	$\nu_{15}\,B_{3g})$
173	183	− 9	228	190	188	− 4	229	187	191 IR, m	$\nu_{14}(B_{2u})$
170	195	− 3	227	190	190	− 8	232	190	198 R, m	$\nu_{12}(B_{2g})$
189	223	− 12	264	220	220	−15	273	228	235 IR, m	$\nu_9(B_{1u})$
227	257	+ 6	313	262	260	+ 9	318	265	251 R, m	$\nu_7(B_{1g})$
242	272	+ 14	305	255	251	− 7	299	251	258 IR, m	$\nu_{18}(B_{3u})$
301	312	+ 5	372	312	312	+ 5	372	312	307 R, s	$\nu_3(A_g)$
485	463	+108[b]	507	424	396	+41[b]	466	362	355 R, w	$\nu_6(B_{1g})$
419	411	+ 16	512	424	408	+13	505	396	395 IR, s	$\nu_{17}(B_{3u})$
447	433	+ 21	521	436	409	− 3	506	400	412 R, s	$\nu_2(A_g)$
563	554	+ 26	670	560	527	− 1	652	517	528 IR, m	$\nu_{13}(B_{2u})$
565	556	+ 3	686	574	560	+ 7	686	564	553 IR, m	$\nu_{16}(B_{3u})$
611	607	+ 9	744	623	614	+16	740	614	598 R, w	$\nu_1(A_g)$
613	620	− 40	791	662	662	+ 2	816	683	660 R, vw	$\nu_{11}(B_{2g})$
619	628	− 27	802	669	669	+14	821	689	655 IR, m	$\nu_8(B_{1u})$

R: Raman; IR: Infrared; s: strong; m: medium; w: weak; v: very.
[a] Not observed, data taken from normal coordinate analysis [12]. [b] Cf. discussion for this assignment.

Scaling factors:

	Torsion (ζ)	S_b-P-S_t (θ)	S_t-P-S_t (α)	$P-P$ (β)	$P-S_t$ (r)	$P-S_b$ (R)
B_1	1.5	1.5	1.3	1.3	1.0	0.9
B_2	0.7	0.7	0.7	0.7	0.7	0.7
B_3	0.7	0.7	0.7	0.7	0.7	0.6

Hence, the dissociation energies should be regarded as very uncertain, and the large differences for the different basis sets should indicate that any interpretation of these numbers may be misleading. There is almost no difference in the geometry by adding a second Gauss function on the 3d-orbitals (STO-5G/2D), the most important change being the shortening of the terminal $P-S_t$ bond.

The overall fit to the experimental geometry for STO-5G* is good enough to justify the vibrational analysis.

The vibrational analysis of A_2B_6 with D_{2h} symmetry results [13] in

$$\Gamma_{vib}(D_{2h}) = 4A_g(R) + A_u(ia) + 2B_{1g}(R) + 3B_{1u}(IR) + 2B_{2g}(R) + 2B_{2u}(IR) + B_{3g}(R) + 3B_{3u}(IR).$$

A different orientation of the axes of the molecule has been chosen in [6] and [12], giving

$$\Gamma_{vib}(D_{2h}) = 4A_g(R) + A_u(ia) + B_{1g}(R) + 3B_{1u}(IR) + 2B_{2g}(R) + 2B_{2u}(IR) + 2B_{3g}(R) + 3B_{3u}(IR).$$

The B_{1g} and B_{1u} vibrations in this work correspond to B_{3g} and B_{3u} in [6] and [12], and *vice versa.*

Table 2 gives a comparison between the calculated frequencies for STO-5G, STO-5G* and STO-5G/2D, unscaled and scaled, and the experimental frequencies. Table 3 summarizes the Potential Energy Distributions (PED) of the best scaled STO-5G* analysis, compared to the results from an earlier reported normal coordinate analysis. The complete force field (terms below 0.01 are omitted) is given in Table 4.

It is surprising how well the simple STO-5G calculation fits the observed vibrational frequencies. Similar good fits have also been obtained for the PS_3^- and the PS_4^{3-} ions [15]. This indicates that such simple calculations may be useful for larger systems such as $P_2S_7^{4-}$, where only small basis sets can be used. The god fit is to a large extent due to the general overestimation of force constants by STO-nG calculations, which is counteracted by the underestimation of the bond strengths when the polarization functions are omitted. It should nevertheless be noted that the deviations between calculated and observed frequencies

Table 3. Potential energy distribution (PED) for $P_2S_6^{2-}$ calculated from the best scaled force field (B_3) of the STO-5G* basis set, along with the observed [6] and calculated [12] vibrational frequencies (cm^{-1}). Notation: See calculation procedure. The PED is based on symmetry force constants.

Species (D_{2h})	Vibrational frequencies			PED[a] [%]
	Obs. [6]	Calc. [12]	STO-5G*	
$\nu_{10}(B_{1u})$		44	28	ζ: 117
$\nu_5(A_u)$		118	94	τ: 68
$\nu_4(A_g)$	169	169	151	β: 49, α: 31, θ: 10
$\nu_{15}(B_{3g})$	184	216	166	θ: 100
$\nu_{14}(B_{2u})$	191	152	188	R: 25, τ: 44
$\nu_{12}(B_{2g})$	198	177	190	θ: 94
$\nu_9(B_{1u})$	235	265	220	α: 44, θ: 10
$\nu_7(B_{1g})$	251	201	251	θ: 108
$\nu_{18}(B_{3u})$	258	241	260	τ: 37, θ: 10
$\nu_3(A_g)$	307	316	312	β: 52, α: 16, r: 15
$\nu_6(B_{1g})$	355	352	396	R: 109, τ: 20
$\nu_{17}(B_{3u})$	395	391	407	R: 61, r: 22
$\nu_2(A_g)$	412	412	408	R: 94, r: 14
$\nu_{13}(B_{2u})$	528	502	527	R: 73
$\nu_{16}(B_{3u})$	553	563	560	r: 81, R: 35
$\nu_1(A_g)$	598	583	614	r: 67, R: 38, β: 34
$\nu_{11}(B_{2g})$	660	646	662	r: 102, θ: 10
$\nu_8(B_{1u})$	655	657	669	r: 100, θ: 12

[a] Contributions below 10% omitted.

Table 4. Scaled Quantum Mechanical (SQM) force constants for the $P_2S_6^{2-}$ ion, calculated at the STO-5G* level, best scaling factors. For the torsional force constants only symmetry force constants are given to avoid ambiguous definition of the interactions.

Diagonal force constants
K_r: 3.500; K_R: 2.100; K_β: 1.771; H_α: 0.749; H_θ: 0.375.

Stretch-stretch, common atom
$f_{R,\beta}$: −0.607; $f_{R,R}$: 0.307; $f_{R,r}$: 0.136; $f_{\beta,r}$: 0.064; $f_{r,r}$: 0.151.

Stretch-stretch, no common atom
$f_{R,R}$: −0.121; $f^1_{r,r}$: 0.040 (S_t trans); $f^2_{r,r}$: 0.060 (S_t cis).

Bend-bend, common central atom
$f^1_{\theta,\theta}$: −0.192 (common S_b); $f^2_{\theta,\theta}$: 0.186 (common S_t); $f^3_{\theta,\theta}$: −0.129 (no common S); $f_{\theta,\alpha}$: −0.171.

Bend-bend, no common central atom
$f^1_{\theta,\theta}$: 0.069 (common S_b, S_t cis); $f^2_{\theta,\theta}$: −0.073 (common S_b, S_t trans); $f^3_{\theta,\theta}$: −0.048 (no common atom); $f_{\alpha,\alpha}$: 0.031.

Stretch-bend
$f_{\beta,\alpha}$: 0.179; $f_{\beta,\theta}$: 0.039; $f_{R,\alpha}$: −0.114 (common atom); $f_{R,\alpha}$: −0.128 (no common atom); $f_{r,\alpha}$: 0.082 (common P); $f^1_{R,\theta}$: −0.114 (common S_b only); $f^2_{R,\theta}$: 0.022 (no common atom); $f^1_{r,\theta}$: −0.112 (common P and S_t); $f^2_{r,\theta}$: 0.072 (common P only).

Torsional symmetry constants
$H_\tau(A_u)$: 0.078; $H_\tau(B_{2u})$: 0.283; $H_\tau(B_{3u})$: 0.078; $h_{\tau,\theta}(A_u)$: 0.036; $h_{\tau,\theta}(B_{2u})$: 0.183; $h_{\tau,\theta}(B_{3u})$: −0.155; $h_{\tau,R}(B_{3u})$: 0.172; $H_\zeta(B_{1u})$: 0.076: $h_{\zeta,r}(B_{1u})$: −0.014.

(also after the scaling) are rather random and the splitting between bands arising from similar vibrations (with mainly the same valence coordinates) may be very wrong (e.g. ν_1, ν_{11}, and ν_8). Finally, the STO-5G calculations indicate the assignment of ν_6 to the weak Raman band at 480 cm^{-1}, but this is contradicted both by the STO-5G* and the normal coordinate analysis given earlier [12]. Hence results on thiophosphates from STO-nG calculations without polarization functions must be treated with utmost care.

The results from the calculations with the STO-5G* basis sets are far more convincing, although a rather drastic scaling is needed. The fit is mostly acceptable with only one scaling factor for all force constants, except for some too high frequencies in the 4–600 cm^{-1} frequency range. Most of these problems are solved by adjustment of only one group of scaling factors for the $P-S_b$ stretching force constants. The deviations show some trends (negative deviations for the low frequencies, positive for the high) and the splitting of bands for vibrations arising from similar vibrations is acceptable. And there is no obvious erroneous assignment, although the deviation for $\nu_6(B_{1g})$ is very large.

The assignment of ν_6 obtained by the STO-5G and STO-5G* calculations is not clear. STO-5G indicates that this vibration should be assigned to the weak Raman band at ca. 480 cm^{-1}, whereas the STO-5G* calculations indicate that the band should be hidden by the strong Raman band at 412 cm^{-1}. And none of the calculations gave any explanation for the Raman band at 355 cm^{-1}.

The very large change in the calculated frequency for ν_6 when including the polarization functions, indicates that this vibration is strongly affected by the d-orbitals. A description of the 3d-orbitals by only one Gaussian primitive may therefore be too crude to facilitate a correct calculation of the frequency of this vibration. To check this hypothesis we rerun the calculations using two contracted Gaussians (STO-2G) for all 3d-orbitals, and ended up with a frequency of ν_6 at 362 cm^{-1}, which is very close to 355 cm^{-1}. The results of the calculations therefore give strong arguments for the assignment of ν_6 to the Raman band at 355 cm^{-1}. This assignment is also supported by normal coordinate analysis [12] (Table 3).

On the other hand, it should be noted that $\nu_4(A_g)$ and $\nu_{15}(B_{3g})$ end up closer to each other for the STO-5G/2D calculation, they are separated by only 6 cm^{-1}. As the deviations between the calculated and the experimental frequencies are large for these two vibrations, one should not completely exclude the possibility that the assignment of these two bands should be reversed.

Related to the surprisingly good fit of the calculated data in comparison to the experimental values with such limited basis sets, there are also further and minor dependencies which should be considered:

I: The calculations only take a single ion into account, and do not look upon interactions between ions, and

II: The calculations assume a full −2 charge on the $P_2S_6^{2-}$ ion, but this is quite probably reduced by the interactions of the counter ions.

These assumptions may introduce errors, but it will not be expected that they produce strong influences on any particular vibration, and hence the given assignment of the vibrational frequencies will be considered reliable.

Furthermore, some of the observed bands may be due to combination bands or overtones, and the fundamental bands may be undetected. This could explain the apparent reversal of ν_{11} and ν_8 in the observed spectra compared to both the *ab initio* calculations and the normal coordinate analysis [12].

Finally, the shape of some of the bands in the IR spectrum show clearly that they are distorted by overlayed reflections [24], especially the strong IR band at 395 cm^{-1}. One should therefore expect this vibration, and some of the other fundamentals, to be at a slightly higher frequency than given in Table 2.

In conclusion, the calculations give strong arguments for the proposed assignment of the vibrational frequencies of the $P_2S_6^{2-}$ ion. The calculations are also strengthened by the correct description for the geometry of the $P_2S_6^{2-}$ ion.

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[1] E. Thilo and G. Ladwig, M.B. Deutsch. Akad. Wiss. Berlin **4,** 720 (1962).
[2] H. Diederich, HL-Zulassungsarbeit, Technical University Clausthal, Clausthal-Zellerfeld 1977, FRG.
[3] C. Wibbelmann, Thesis, Technical University Clausthal, Clausthal-Zellerfeld 1982, FRG.
[4] P. Toffoli, P. Khodadad, and N. Rodier, Acta Cryst. **B 34,** 3561 (1978).
[5] C. Wibbelmann, W. Brockner, B. Eisenmann, and H. Schäfer, Z. Naturforsch. **38 b,** 1575 (1983).
[6] W. Brockner, R. Becker, B. Eisenmann, and H. Schäfer, Z. anorg. allg. Chem. **520,** 51 (1985).
[7] M. Bouchetiere, P. Toffoli, P. Khodadad, and N. Rodier, Acta Cryst. **B 34,** 384 (1978).
[8] R. Becker and W. Brockner, Z. Naturforsch. **39 a,** 1120 (1984).
[9] I. R. Beattie and J. R. Horder, J. Chem. Soc. A 2655 (1969).
[10] V. A. Maroni, D. M. Gruen, R. L. McBeth, and E. J. Cairns, Spectrochim. Acta **A 26,** 418 (1970).
[11] H. W. Roesky, R. Ahlrichs, and S. Brode, Angew. Chem. **98,** 91 (1986).
[12] L. Ohse and W. Brockner, Z. Naturforsch. **43 a,** 494 (1988).
[13] T. Tomita, C. E. Sjøgren, P. Klæboe, G. N. Papatheodoru, and E. Rytter, J. Raman Spectrosc. **14,** 415 (1983).
[14] P. Pyykkö, Chem. Comm. **12,** 933 (1990).
[15] M. Ystenes, W. Brockner, and F. Menzel, Vibrational Spectroscopy, submitted.
[16] M. Ystenes, W. Brockner, and F. Menzel, Proc. 8th FTS Conf. Lübeck 1991, in press.
[17] F. Menzel, W. Brockner, and M. Ystenes, J. Raman Spectrosc., to be submitted.
[18] GAMESS, distributed by M. Schmidt, North Dakota State University and S. Elbert, Iowa State University, 1988.
[19] A. Hinchcliffe, *Ab initio* Determination of Molecular Properties, Adam Hilger, Bristol 1987.
[20] A. Hinchcliffe, Computational Quantum Chemistry, John Wiley & Sons, Chichester 1988.
[21] MOLVIB, T. Sundius, Institute of Physics, University of Helsinki, Finland 1988.
[22] GAMFORCE, Ø. Bache, Institute of Inorganic Chemistry, NTH, Trondheim, Norway 1991.
[23] See e.g. E. Fjogstad and M. Ystenes, Spectrochim. Acta **46 A,** 47 (1990).
[24] E. Rytter, Spectrochim. Acta **43 A,** 523 (1987).